

# Diesel Fuel Sulfur Testing, Sampling Methods, and Requirements

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# *Designated and Alternative Test Methods Under Highway Rule\**

Fuel S Level	Designated Test Method	Alternative Test Methods
15 ppm	ASTM** D 6428-99 (D 6920-03)	ASTM D 5453-03a
		ASTM D 3120-03a
		ASTM D 2622-03
500 ppm	ASTM D 2622-03	ASTM D 5453-03a
		ASTM D 6428-99
		ASTM D 4294-03

\*Designated and Alternative Test Methods for 15 ppm MV and NRLM fuel valid only through 12/27/04.

\*\*American Society for Testing and Materials



# *Sulfur Sampling and Testing – What's New*

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- Any VCSB or non-VCSB method that meets specified performance criteria under 40 CFR 80.584 and 80.585 can be used, including on-line methods.
- For 15 ppm ULSD, just using a designated “approved” method is not sufficient.
- Lab has to qualify each individual method it wants to use on lab specific basis using the Qualification Criteria in 40 CFR 80.584.
- Non-VCSB method good for only 5 years unless VCSB acceptance is obtained.
- Allows for greater flexibility in instrument selection and encourages the development and use of better instrumentation.



# *Sulfur Sampling and Testing – What's New cont.*

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- Sampling (same as highway rule)
  - ASTM D 4057-95 – manual sampling
  - ASTM D 4177-95 – automatic sampling
- Testing
  - Method approval on a laboratory/facility-specific basis using Performance Based Measurement System
  - Qualification criteria
    - Precision
      - 20 repeat tests over 20 days on samples taken from a single commercially available diesel fuel
      - Standard deviation must be less than
        - » 0.72 ppm for 15 ppm sulfur diesel fuel
        - » 9.68 ppm for 500 ppm sulfur diesel fuel



# *Sulfur Sampling and Testing – Qualification Criteria cont.*

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- Accuracy
  - Two continuous series of 10 repeat tests on two commercially-available gravimetric sulfur standards
  - Mean of test results may not deviate from the Accepted Reference Value of the standard by more than
    - » 0.54 ppm for 15 ppm sulfur diesel fuel
    - » 7.26 ppm for 500 ppm sulfur diesel fuel
  - 10 tests are required on each of two sulfur levels as follows;
    - » 1-10 ppm and 10-20 ppm for 15 ppm sulfur diesel fuel
    - » 100-200 ppm and 400-500 ppm for 500 ppm sulfur diesel fuel
  - Quality control provisions based on ASTM D 6299-02
- P&A standard deviation criteria were based on 2002 ASTM Round Robin results using ASTM D 3120-96 for 15 ppm; D 2622 for 500 ppm.



# *Methods that May Meet Precision & Accuracy Requirements*

<b>ASTM D 3120–03a</b>	Standard Test Method for Trace Quantities of Sulfur in Light Liquid Petroleum Hydrocarbons by Oxidative Microcoulometry
<b>ASTM D 5453–03a</b>	Standard Test Method for Determination of Total Sulfur in Light Hydrocarbons, Motor Fuels and Motor Oils by Ultraviolet Fluorescence
<b>ASTM D 6920-03 (D 6428-99)</b>	Test Method for Total Sulfur in Liquid Aromatic Hydrocarbons and Their Derivatives by Oxidative Combustion and Electrochemical Detection
<b>ASTM D 7039-04</b>	Test Method for Sulfur in Gasoline and Diesel Fuel by Monochromatic Wavelength Dispersive X-ray Fluorescence Spectrometry
<b>ASTM D 2622–03</b>	Standard Test Method for Sulfur in Petroleum Products by Wavelength Dispersive X-ray Fluorescence Spectrometry

- EPA is in process of developing guidance template for lab qualification.



# *Current Methods Status*

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- Current reproducibility of the test methods in ASTM Ultra Low Sulfur Diesel (ULSD) Interlaboratory Crosscheck Program (ILCP) is greater than 2 ppm for 15 ppm sample.
- April 2004 ILCP results by method are as follows:
  - D 3120-03a is 2.57 ppm
  - D 5453-03a 3.94 ppm
  - D 2622-03 is 5.92 ppm
- Improvements need to be made to improve reproducibility
  - 1) Standards improvement
    - National Institutes of Standards and Technology (NIST) blanks and SRMs
  - 2) Methods improvement
    - Address ASTM ULSD ILCP data
    - Aid labs in measurement process



# *Standards Improvement*

- NIST is currently developing new natural matrix standards with improved accuracy

SRM #	Certified Value (ppm)	Uncertainty (ppm)	Availability
1616b*	8.41	$\pm 0.12$	12/04
2770*	41.57	$\pm 0.39$	12/04
2771*	<0.5	$\pm 0.2$	1/05
2723a**	11.0	$\pm 1.1$	12/03

\* Official certified values and uncertainties will be released shortly.

\*\* NIST is considering the re-certification of the  $11.0 \pm 1.1$  ppm S in Diesel Fuel Oil to improve uncertainty using improved techniques.





# *Standards Improvement cont.*

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- NIST new approach to blending SRMs.
- Should allow user to create “custom” SRMs with uncertainty better than  $\pm 0.5$  ppm.
- Paper will be presented December 8<sup>th</sup> at ASTM D02 conference.
- When these SRMs are all available and used to full potential, reproducibility should improve.
- NIST has offered to verify ILCP ULSD sample values; funding needs to be established.



# *Methods Improvement*

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- We believe outlier labs may be pushing ASTM ILCP reproducibility high.
- Request to ASTM for lab code information to correlate individual lab results from month-to-month.
- ASTM has stated that access to data is possible.



# *Methods Improvement cont.*

- Reproducibility is clearly improving over time:

Method	2002 RR Reproducibility (~ 15 ppm sample)	2004 ILCP Reproducibility (~ 15 ppm sample)
D 5453	6.26 ppm	3.94 ppm
D 3120	8.07 ppm	2.57 ppm

- Based on improvements, EPA believes that reproducibility will be 2 ppm or better by the time ULSD is introduced.
- EPA will work one-on-one with labs
- Any laboratory can send ULSD samples to EPA NVFEL for analysis
- API has agreed to have their test methodologies workgroup work with EPA to make improvements to test methods to improve reproducibility.



# *For More Information...*

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Visit EPA's Clean Diesel Website:  
<http://www.epa.gov/cleandiesel/>

Send ULSD Samples (1 liter) to:  
US EPA, NVFEL  
Attn: Nancy Tschirhart  
2565 Plymouth Road  
Ann Arbor, MI 48105

